

Phenanthraquinone is per-hydrogenated over platinum at 25° to a perhydro-9,10-dihydroxyphenanthrene, m. p. 174°, and over nickel at 160° to a mixture of three stereoisomers of the above, with m. p.'s 174° (not identical with the platinum product), 155 and 184°, respectively. The first three products have the *cis-syn-cis* configuration and may be oxidized to *cis-syn-cis*-perhydrodiphenic acid. The glycol of m. p. 184°, which is obtained in very small yield, has a *cis-syn-trans*

configuration as it gives the *cis-syn-trans*-perhydrodiphenic acid on oxidation. The three *cis-syn-cis* glycols differ in the orientation of their hydroxyl groups and represent all the forms with this skeletal configuration which are theoretically possible. Over nickel at 120°, phenanthraquinone yields mainly Skita's decahydro-9,10-dihydroxyphenanthrene.

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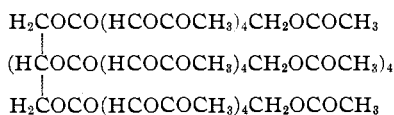
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

O-Pentaacetyl-*d*-gluconates of Polyhydric Alcohols and Cellulose¹

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To our knowledge, only the methyl³ and ethyl⁴ esters of *d*-gluconic acid pentaacetate have been reported. The object of the present investigation was to prepare and characterize the O-pentaacetyl-*d*-gluconates of polyhydric alcohols and cellulose. Such esters were prepared from ethylene glycol, propanediol-1,3 (trimethylene glycol), bis-(2-hydroxyethyl) ether (diethylene glycol), glycerol, (*dextro*)-sorbitol, *d*-mannitol, α -methyl-*d*-glucoside, mercerized cotton linters and a modified cellulose acetate by reaction of these substances with an excess of *d*-gluconyl chloride pentaacetate in pyridine solution.

Ethylene glycol, propanediol-1,3 and bis-(2-hydroxyethyl) ether formed crystalline di-esters. Glycerol, (*dextro*)-sorbitol, *d*-mannitol and α -methyl-*d*-glucoside yielded fully esterified products in the form of colorless, amorphous powders. This lack of crystallizing power is not surprising, as the molecular weights of these esters are very high. Thus the ethylene glycol derivative has a molecular weight of 839 and the hexitol derivative (C₁₀₂H₁₃₄O₇₂, shown below) has a molecular weight of 2512.



In the case of mercerized cotton linters, pyri-

dine was found unsatisfactory as a reaction medium because the intense coloration developed by the acid chloride and pyridine, even at room temperature, was very strongly adsorbed on the fibers. Of several other tertiary bases tried as a substitute for pyridine in the reaction with cellulose, triethylamine in an inert solvent was found most satisfactory for the elimination of color. Using triethylamine as the base, a cream-colored, fibrous cellulose O-pentaacetyl-*d*-gluconate was obtained containing 0.45 O-pentaacetyl-*d*-gluconyl group per anhydroglucose unit. In pyridine, a modified cellulose acetate (1.72 acetyl group per anhydroglucose unit) yielded a mixed ester containing 0.75 O-pentaacetyl-*d*-gluconyl group per anhydroglucose unit, while with triethylamine in chloroform a product with 0.33 O-pentaacetyl-*d*-gluconyl groups was produced. The former was obtained as a cream-colored powder that was acetone and chloroform soluble and formed brittle films. The latter product was colorless, was acetone and chloroform soluble, and formed strong, flexible, transparent films.

Experimental

Preparation of the O-Pentaacetyl-*d*-gluconates of Several Polyhydric Alcohols.—The anhydrous polyhydric alcohol (0.5 g.) was dissolved in dry pyridine (50 cc.). Gluconyl chloride pentaacetate^{4b} (9 g.) was quickly ground and added in approximately 1-g. portions to the solution with shaking. The mixture became warm and slowly turned deep orange in color. A crystalline water-soluble pyridine-complex separated after a few minutes. After standing overnight, the reaction mixture was diluted to incipient turbidity with water and the material crystallized. More water was added gradually until the volume was about 1 liter. This procedure was followed for the

(1) Presented in essentially the present form before the Division of Cellulose Chemistry at the 101st Meeting of the American Chemical Society, St. Louis, Missouri, April 9, 1941.

(2) Du Pont Cellulose Research Fellow.

(3) G. B. Robbins and F. W. Upson. *THIS JOURNAL*, **62**, 1076 (1940).

(4) (a) F. Volpert, *Ber.*, **19**, 2622 (1886); (b) R. T. Major and E. W. Cook. *THIS JOURNAL*, **68**, 2474, 2477 (1936).

TABLE I
 O-PENTAACETYL-*D*-GLUCONATES OF POLYHYDRIC ALCOHOLS

Substance, (O-pentaacetyl- <i>D</i> -gluconate)	Formula	State	M. p., °C.	[α] _D ²⁰ , c 4, abs. CHCl ₃	Yield, ^a g., pure product	Analyses, %					
						Calculated		Saponi- fication value ^b	Found		Saponi- fication value ^b
C	H	C	H	C	H						
Ethylene glycol di-	C ₂ H ₄ O ₂ (C ₆ H ₉ O ₆ (COCH ₃) ₅) ₂	crystalline	94-95	+15°	5.2	48.69	5.53	14.3	48.50	5.63	14.3
Propanediol-1,3 di-	C ₃ H ₆ O ₂ (C ₆ H ₉ O ₆ (COCH ₃) ₅) ₂	crystalline	88-89	+18.5	4.5	49.30	5.68	14.1	49.22	5.84	14.2
Bis(2-hydroxyethyl) ether di-	C ₄ H ₈ O ₃ (C ₆ H ₉ O ₆ (COCH ₃) ₅) ₂	crystalline	111-112	+12	3.8	48.98	5.71	13.6	48.70	5.78	13.7
Glycerol tri-	C ₃ H ₅ O ₃ (C ₆ H ₉ O ₆ (COCH ₃) ₅) ₃	white	58-65 ^c	+20	4.5	48.74	5.45	14.3	48.66	5.60	14.3
(<i>dextro</i>)-Sorbitol hexa-	C ₆ H ₅ O ₆ (C ₆ H ₉ O ₆ (COCH ₃) ₅) ₆	powder	65-78 ^c	+30	4.0	48.75	5.38	14.3	49.02	5.29	14.3
<i>d</i> -Mannitol hexa-	C ₆ H ₈ O ₆ (C ₆ H ₉ O ₆ (COCH ₃) ₅) ₆	white powder	65-78 ^c	+37	2.0	48.75	5.38	14.3	48.68	5.33	14.3
α -Methyl- <i>D</i> -gluco- pyranoside tetra-	C ₇ H ₁₀ O ₆ (C ₆ H ₉ O ₆ (COCH ₃) ₅) ₄	white powder	68-72 ^c	+57	2.0	48.86	5.42	13.7	49.01	5.41	13.7

^a From 0.5 g. of the polyhydric alcohol. ^b Method of A. Kunz and C. S. Hudson, THIS JOURNAL, 43, 1982 (1926); recorded as cc. 0.1 *N* NaOH per 100 mg. of substance. ^c Softening point.

first three products of Table I, where the alcohols were ethylene glycol, trimethylene glycol (propanediol-1,3) and diethylene glycol (bis-(2-(hydroxyethyl) ether). Crystalline products were obtained in each case and were purified by recrystallization from ethanol (decolorizing charcoal) and methanol-water. It was found that the addition of ethylene glycol to a solution of gluconyl chloride pentaacetate in pyridine gave no water-insoluble product and the solution became nearly black in color.

For the last four products of Table I (esters of glycerol, *dextro*-sorbitol, *d*-mannitol and α -methyl-*D*-glucopyranoside), the final products were obtained in the form of white, amorphous powders that resisted crystallization but were of analytical purity. These substances were isolated by pouring the reaction mixture through a small orifice into 800 cc. of a rapidly stirred mixture of ice and water. Purification was effected by solution in acetone (decolorizing charcoal) and precipitation by the addition of water. Colloidal solutions sometimes formed which were easily broken by the addition of a small amount of electrolyte. Drying was carried out slowly and below 45°. The esters of mannitol and of α -methyl-glucoside were purified from methanol (decolorizing charcoal)-water. In the case of mannitol, the reaction mixture was heated initially to 50° for five minutes and was then kept at room temperature overnight. The α -methyl-glucoside reaction mixture was kept at room temperature for seven days. All of the esters were soluble in the common solvents except petroleum ether and water.

Cellulose O-Pentaacetyl-*D*-gluconate.—High viscosity cotton linters⁵ (0.5 g.) were mercerized for one hour at 20° in 25 cc. of 18% sodium hydroxide solution. The fibers were washed with water until free of alkali and placed in 50 cc. of dry nitrobenzene after solvent interchange with acetone and nitrobenzene. Triethylamine (0.7 cc.) and gluconyl chloride pentaacetate (5.2 g.) were added and the mixture heated at 80° for sixteen hours. The fibers were well dispersed but undissolved at the end of this time. The liquor showed no turbidity when diluted with large amounts of ethanol. The fibrous product was collected, thoroughly washed with acetone, water and ethanol, and then dried; yield 0.70 g. It was cream colored and resembled the original linters in texture.

(5) Furnished by the courtesy of the Hercules Powder Co., Hopewell, Va.

A saponification was made according to the procedure of Malm and Clarke⁶ for cellulose acetate. A blank was run on the solvent and on gluconic acid pentaacetate and corrections were made for a small absorption of alkali by the cellulose. The material was prepared for analysis by drying at 100° for three hours. The saponification equivalents found were 124.3 and 125.0 (8.04 cc. and 8.00 cc. of 0.1 *N* NaOH per 100 mg.). These correspond to 0.45 and 0.44 O-pentaacetyl-*D*-gluconyl group per anhydroglucose unit.

Cellulose Acetate O-Pentaacetyl-*D*-gluconate. Procedure A.—Cellulose acetate⁷ (1.72 acetyl groups per anhydroglucose unit, 1.0 g.) was dissolved in 50 cc. of dry pyridine with 6.0 g. of gluconyl chloride pentaacetate and then kept at room temperature for one hundred and twenty hours. Upon pouring the mixture into rapidly stirred, cold water, a flesh-colored precipitate was obtained. The product was purified by precipitation with water from acetone solution and from pyridine solution (decolorizing charcoal), giving a cream-colored, amorphous powder; yield 1.53 g., spec. rot. +2.5° (24°, D line, *c* 3, CHCl₃), spec. rot. -10° (21°, *c* 1.5, dry pyridine). The substance was soluble in acetone, pyridine, glacial acetic acid, chloroform and warm tetrachloroethane. It was incompletely soluble in warm 75% ethanol. It formed dark yellow, brittle films. The original cellulose acetate was insoluble in acetone and chloroform, but was easily soluble in pyridine and warm 75% ethanol, and its specific rotation was -13° (24°, D line, *c* 3, dry pyridine).

The saponification equivalents⁸ determined in acetone were 84.1 and 84.0 (11.89 cc. and 11.91 cc. 0.1 *N* NaOH per 100 mg.). These values correspond to 0.75 O-pentaacetyl-*D*-gluconyl group per anhydroglucose unit.

Procedure B.—Another sample of the same cellulose acetate (1.0 g.) was placed in 60 cc. of absolute chloroform with 1.0 cc. of triethylamine and 5.2 g. of gluconyl chloride pentaacetate and heated for forty-two hours at 60°. The mixture became orange in a short time and the cellulose acetate slowly went into solution. The solution was filtered and poured into 300 cc. of absolute ethanol, giving a gelatinous precipitate, which, after thorough washing with ethanol and water, dried to a colorless, amorphous powder;

(6) C. J. Malm and H. T. Clarke, THIS JOURNAL, 51, 274 (1929).

(7) Furnished through the courtesy of the Du Pont Rayon Co., Waynesboro, Va.

yield 1.22 g., spec. rot. $+1^\circ$ (24° , D line, c 3.5, CHCl_3) and -9° (23° , D line, c 3.5, dry pyridine).

The product was soluble in acetone, chloroform, glacial acetic acid, pyridine, warm dioxane and benzene. It dissolved somewhat in warm 75% ethanol accompanied by strong swelling. It formed strong, flexible, colorless films from acetone or chloroform solutions.

The saponification equivalents⁶ determined in acetone were 99.1 and 99.7 (10.09 cc. and 10.03 cc. 0.1 *N* NaOH per 100 mg.). These values correspond to 0.33 and 0.29 O-pentaacetyl-*d*-gluconyl groups per anhydroglucose unit. Repeated esterification of cellulose acetate under conditions similar to those described above did not raise the substitution above 0.37 O-pentaacetyl-*d*-gluconyl group per anhydroglucose unit.

Summary

1. Crystalline di-(O-pentaacetyl-*d*-gluconates) of ethylene glycol, propanediol-1,3 and bis-(2-hydroxyethyl) ether have been prepared by the reaction of the corresponding glycol with *d*-

gluconyl chloride pentaacetate in pyridine.

2. Under similar conditions glycerol, (*dextro*)-sorbitol, *d*-mannitol and α -methyl-*d*-glucoside formed fully esterified O-pentaacetyl-*d*-gluconates in the form of colorless, amorphous powders.

3. Mercerized cotton linters were esterified in the presence of triethylamine and nitrobenzene, forming a fibrous product containing 0.4 O-pentaacetyl-*d*-gluconyl group per anhydroglucose unit.

4. A modified cellulose acetate (1.72 acetyl groups per anhydroglucose unit) in pyridine gave a mixed ester containing 0.7 O-pentaacetyl-*d*-gluconyl group per anhydroglucose unit and in chloroform and triethylamine, a mixed ester containing 0.3 O-pentaacetyl-*d*-gluconyl group per anhydroglucose unit was formed.

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The Glyoxalines. II. A Study of the Reaction between Benzamidine and Phenylglyoxal

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A reaction between benzamidine and phenylglyoxal was reported by Kunckell and Bauer¹ in which a compound described as "phenacal benzamidine" (m. p. 224°) was isolated. When repeated by us the reaction proceeded exactly as described by them. The product obtained, recrystallized from ethyl alcohol, melted at 225° . Nitrogen analyses, however, failed to check the value for "phenacal benzamidine." The value obtained (13.65%) was so close to the value for kyanphenin (13.60%) that a melting point of the mixture was taken. The melting point found was 228° (m. p. of pure kyanphenin 230 – 231°). The solubilities and physical appearance of "phenacal benzamidine" and kyanphenin were also identical. The experiment was repeated many times with the same result. Hence, the work of Kunckell and Bauer was considered to be in error and the reaction between benzamidine and phenylglyoxal was re-investigated.

The products obtained from the reaction between benzamidine and phenylglyoxal under different conditions are shown in Chart I. Compound I was formed when the two reactants were

treated with base in cold alcohol solution. Recrystallized from ethyl acetate, the product gave analyses corresponding to the formula $\text{C}_{17}\text{H}_{18}\text{O}_3\text{N}_2$. Since the compound formed readily in cold solution, it appeared likely that it was a simple addition product. The compound contains one-half molecule of ethyl acetate of crystallization.

Compound I is converted to Compound II by dissolving in basic solution, heating for a short time, then carefully neutralizing with acid. Recrystallized from dioxane, the analyses correspond to a compound $\text{C}_{17}\text{H}_{16}\text{O}_2\text{N}_2$.² The compound contains one-half molecule of dioxane of crystallization as proved by a cryoscopic determination.

When a basic solution of either Compound I or II is treated with an excess of hydrochloric acid, a voluminous precipitate of the hydrochloride of Compound III is formed. This compound is very unstable in the absence of acids. Analyses gave results corresponding to the formula $\text{C}_{15}\text{H}_{14}\text{O}_2\text{N}_2\cdot\text{HCl}$.

(2) In the first paper of this series [Fisher, Ekeley and Ronzio, *THIS JOURNAL*, **64**, 1434 (1942)] it has been shown that phenylglyoxal and urea react to form 4-phenyl-hydantoin. Should a similar reaction take place when benzamidine is used instead of urea, the formula for Compound II, would then be the second structure shown on Chart I.

* Now with Eastman Kodak Co.

(1) Kunckell and Bauer, *Ber.*, **34**, 3029 (1901)